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## Some unusual organo-zinc and -mercury compounds. The crystal structures of the compounds $[(\text{HOME}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$ , $[(\text{MeOME}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$ , and $[(\text{MeOME}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Hg}$

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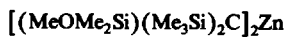
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### Abstract

The preparation of the novel mercurial  $[(\text{MeOME}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Hg}$  is described. X-ray diffraction studies show that the molecules of this compound and its zinc analogue are centrosymmetric (and the C–M–C linkage thus linear), but in the former the OMe group is directed away from the metal atom whereas in the latter it lies in towards the metal, with an  $\text{O}\cdots\text{Zn}$  distance of 2.93 Å. In crystals of  $[(\text{HOME}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$  there is hydrogen bonding between the two oxygen atoms within each molecule, and hydrogen bonding between two molecules to give discrete dimers. Because of the hydrogen bonding the C–Zn–C linkage is slightly bent (the angle is  $175.9(1)^\circ$ ), and the geometries of the two  $(\text{HOME}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}$  groups are significantly different.

### Introduction

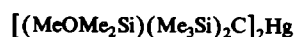
We have recently shown that substitutions, some involving powerful electrophilic reagents, can be carried out at the Si–X bonds in compounds of the type  $[(\text{XMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$  without cleavage of the C–Zn bonds [1], and two compounds made in this way were the dimethoxy compound **1** and the diol **2**. We thought it of interest to determine their crystal structures, in order (a) to see whether there was any intramolecular interaction between the O atoms and the zinc atom (as in  $[\text{MeO}(\text{CH}_2)_4]_2\text{Zn}$  [2]), and (b), in the case of **2**, to examine the nature of any hydrogen bonding between the SiOH groups (a subject in which we have an active interest [3]). For comparison we also determined the crystal structure of the mercury compound **3**, since it is known that dialkylmercury derivatives are less likely than their dialkylzinc analogues to bind to external oxygen- or nitrogen-centred ligands, as illustrated by the structures of the compounds  $[(\text{NC}_3\text{H}_4)(\text{SiMe}_3)_2\text{C}]_2\text{M}$  (M = Zn, Cd, or Hg) [4].



(1)



(2)



(3)

## Results and discussion

### Preparation and crystal structure of 3

This compound was made by treatment of  $\text{HgBr}_2$  with the lithium reagent  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CLi}$ , itself made from  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCl}$  and  $\text{BuLi}$  at low temperature (cf. ref. 5).

In crystals of **3** all three Si atoms of each  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}$  group are disordered between two sites, with relative occupancies of 0.75 and 0.25, in a way noted previously for various compounds containing  $(\text{Me}_3\text{Si})_3\text{C}$  groups [6], and this reduces the accuracy of the derived geometrical parameters. The structure of the dominant orientation is shown in Fig. 1, and the bond lengths and angles for both orientations are given in Table 1. The molecule is centrosymmetric, and the  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}$  groups are staggered in antiperiplanar fashion. Within the accuracy of the data, the C–Hg bond length is not significantly different from that in  $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{Hg}$  [7]. It is evident from Fig. 1 that there is no question of interaction between the Hg atom and the OMe groups, which are clearly directed away from the metal. The only other comment necessary is that the seemingly abnormally low value of the Si–O–Me angle,  $110(2)^\circ$  and high value of the Si–O bond length (1.90(3) Å) are unreliable because of the disorder.

### Crystal structure of compound 1

The structure of the zinc compound **1** is shown in Fig. 2, and the bond lengths and angles are listed in Table 2. The overall structure is very similar to that of **3**, except for the disposition of the OMe groups (see below). The C–Zn bond length is somewhat greater than those in the diol **2**, but comparable with those in the related compounds  $[(\text{XMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$  (Table 3); it is significantly smaller than those

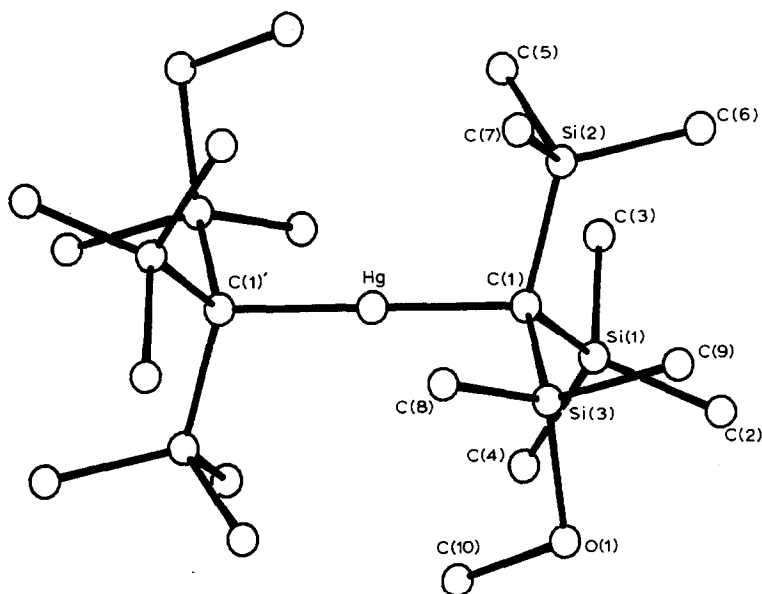


Fig. 1. Structure of  $[(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Hg}$ , **3**, with atom numbering.

Table 1

Intramolecular distances (Å) and angles (°) for **3** with estimated standard deviations in parentheses

<b>(a) Bonds</b>			
Hg–C(1)	2.07(2)	Si(1)–C(1)	1.87(2)
Si(1)–C(2)	1.83(3)	Si(1)–C(3)	2.02(4)
Si(1)–C(4)	1.86(4)	Si(2)–C(1)	1.86(3)
Si(2)–C(5)	1.82(3)	Si(2)–C(6)	1.91(3)
Si(2)–C(7)	2.03(4)	Si(3)–O(1)	1.90(3)
Si(3)–C(1)	1.96(2)	Si(3)–C(8)	1.87(3)
Si(3)–C(9)	2.00(3)	O(1)–C(10)	1.77(8)
Si(1a)–O(1)	2.08(4)	Si(1a)–C(1)	1.81(3)
Si(1a)–C(2)	1.97(4)	Si(1a)–C(4)	1.92(4)
Si(2a)–C(1)	1.88(3)	Si(2a)–C(7)	1.98(4)
Si(2a)–C(8)	1.97(5)	Si(2a)–C(9)	2.18(4)
Si(3a)–C(1)	1.98(4)	Si(3a)–C(3)	2.04(4)
Si(3a)–C(5)	1.67(4)	Si(3a)–C(6)	2.04(4)
<b>(b) Angles</b>			
C(1)–Si(1)–C(2)	117(1)	C(1)–Si(1)–C(3)	106(1)
C(1)–Si(1)–C(4)	112(1)	C(2)–Si(1)–C(3)	111(2)
C(2)–Si(1)–C(4)	105(1)	C(3)–Si(1)–C(4)	105(2)
C(1)–Si(2)–C(5)	110(1)	C(1)–Si(2)–C(6)	114(1)
C(1)–Si(2)–C(7)	108(1)	C(5)–Si(2)–C(6)	101(2)
C(5)–Si(2)–C(7)	111(1)	C(6)–Si(2)–C(7)	111(2)
O(1)–Si(3)–C(1)	108(1)	O(1)–Si(3)–C(8)	115(2)
O(1)–Si(3)–C(9)	105(2)	C(1)–Si(3)–C(8)	109(1)
C(1)–Si(3)–C(9)	110(1)	C(8)–Si(3)–C(9)	109(1)
Si(3)–O(1)–C(10)	110(2)	Hg–C(1)–Si(1)	110(1)
Hg–C(1)–Si(2)	106.8(9)	Hg–C(1)–Si(3)	106(1)
Si(1)–C(1)–Si(2)	112(1)	Si(1)–C(1)–Si(3)	110(1)
Si(2)–C(1)–Si(3)	112(1)	O(1)–Si(1a)–C(1)	107(2)
O(1)–Si(1a)–C(2)	111(2)	O(1)–Si(1a)–C(4)	116(2)
C(1)–Si(1a)–C(2)	114(2)	C(1)–Si(1a)–C(4)	112(1)
C(2)–Si(1a)–C(4)	97(2)	C(1)–Si(2a)–C(7)	109(2)
C(1)–Si(2a)–C(8)	109(2)	C(1)–Si(2a)–C(9)	105(1)
C(7)–Si(2a)–C(8)	115(2)	C(7)–Si(2a)–C(9)	120(2)
C(8)–Si(2a)–C(9)	99(2)	C(1)–Si(3a)–C(3)	102(2)
C(1)–Si(3a)–C(5)	112(2)	C(1)–Si(3a)–C(6)	104(2)
C(3)–Si(3a)–C(5)	118(2)	C(3)–Si(3a)–C(6)	119(2)
C(5)–Si(3a)–C(6)	102(2)		

of the C–metal bonds in related derivatives of other metals, including the anions  $\{[(\text{Me}_3\text{Si})_3\text{C}]_2\text{M}\}^-$  (M = Li, Cu, or Ag) (see Table 3).

At first sight it seems that there is some coordination between the O and Zn atoms, the OMe group being orientated so that the lone pairs of the O atoms point towards the Zn atom and the Si–OMe bond being bent in towards the Zn atom, with the C(1)–Si(3)–O angle only  $104.4(2)^\circ$ , compared with the associated C(1)–Si(3)–C(8) and C(1)–Si(3)–C(9) angles of  $115.8(2)^\circ$  and  $114.1(3)^\circ$ , respectively, and with, for example, the C(1)–Si(2)–C(6) angle of  $111.9(2)^\circ$ . (The C(1)–Zn $\cdots$ O angle is  $66(1)^\circ$ ). However, the O $\cdots$ Zn distance is  $2.932(4)^\circ$ , close to the sum of the relevant van der Waals radii, and it seems likely that the orientation of the OMe groups reflects minimization of steric strain rather than definite but weak coordinative interaction. Nevertheless, it is attractive to attribute the difference between the

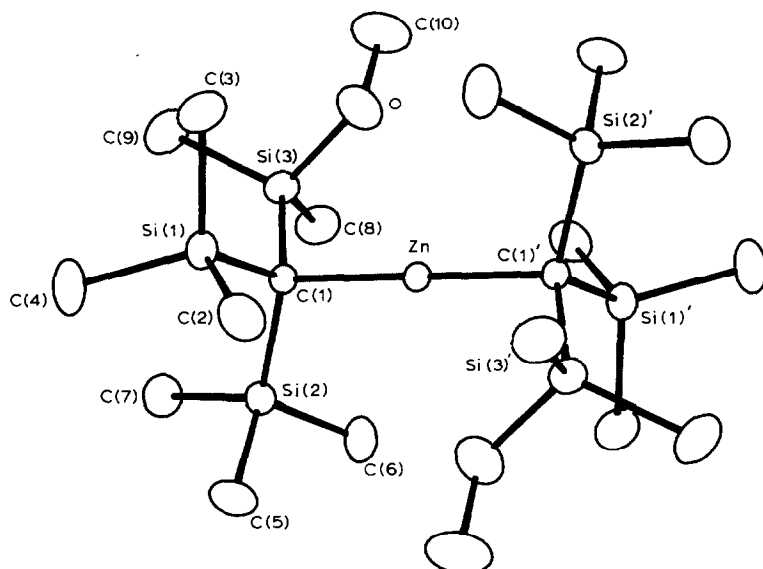


Fig. 2. Structure of  $[(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$ , **1**, with atom numbering.

structures of **1** and **3** to the fact that the Zn atom can tolerate a close approach of the oxygen lone pairs more readily than can the Hg atom.

A feature of interest is that if one of the  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}$  groups is rotated about the C–Zn to bring the two O atoms into eclipsed positions the  $\text{O}\cdots\text{O}$

Table 2

Intramolecular distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in **1**, with estimated standard deviations in parentheses

(a) Bonds			
Zn–C(1)	1.980(4)	Si(1)–C(1)	1.877(4)
Si(1)–C(2)	1.864(6)	Si(1)–C(3)	1.874(6)
Si(1)–C(4)	1.880(6)	Si(2)–C(1)	1.878(4)
Si(2)–C(5)	1.852(6)	Si(2)–C(6)	1.861(6)
Si(2)–C(7)	1.877(5)	Si(3)–O	1.674(3)
Si(3)–C(1)	1.853(4)	Si(3)–C(8)	1.860(6)
Si(3)–C(9)	1.879(6)	O–C(10)	1.401(9)
(b) Angles			
C(1)–Si(1)–C(2)	112.0(2)	C(1)–Si(1)–C(3)	112.7(2)
C(1)–Si(1)–C(4)	113.3(2)	C(2)–Si(1)–C(3)	105.1(2)
C(2)–Si(1)–C(4)	106.2(3)	C(3)–Si(1)–C(4)	107.1(3)
C(1)–Si(2)–C(5)	113.9(2)	C(1)–Si(2)–C(6)	111.9(2)
C(1)–Si(2)–C(7)	112.7(2)	C(5)–Si(2)–C(6)	104.8(3)
C(5)–Si(2)–C(7)	106.0(2)	C(6)–Si(2)–C(7)	106.8(2)
O–Si(3)–C(1)	104.4(2)	O–Si(3)–C(8)	106.2(2)
O–Si(3)–C(9)	110.2(2)	C(1)–Si(3)–C(8)	115.8(2)
C(1)–Si(3)–C(9)	114.1(3)	C(8)–Si(3)–C(9)	105.8(3)
Si(3)–O–C(10)	122.0(4)	Zn–C(1)–Si(1)	105.3(2)
Zn–C(1)–Si(2)	108.3(2)	Zn–C(1)–Si(3)	104.6(2)
Si(1)–C(1)–Si(2)	112.9(2)	Si(1)–C(1)–Si(3)	112.9(2)
Si(2)–C(1)–Si(3)	112.2(2)		

Table 3

Metal-carbon bond lengths (Å) in the anions  $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{M}^-$  ( $\text{M} = \text{Li}, \text{Cu}, \text{Ag}$ ) and the compounds  $[(\text{XMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{M}$

M	X	Bond length(s)	Ref.
Li	Me	2.16(1), 2.20(1)	9
Cu	Me	2.03(1), 2.07(1)	10
Ag	Me	2.162(7), 2.198(7)	11
Hg	Me	2.142(4)	7
Hg	MeO	2.07(2)	this work
Mg	Me	2.116(2)	12
Mn	Me	2.102(4)	13
Cd	$\text{CH}_2=\text{CH}$	2.172(3)	14
Zn	Cl	1.983(7)	15
Zn	$\text{CF}_3\text{CO}_2$	1.974(3)	16
Zn	MeO	1.980(4)	this work
Zn	HO	1.965(2), 1.970(2)	this work

distance is only 2.38 Å, some 0.6 Å below twice the van der Waals radius for oxygen, and the distance between the attached carbon atoms is only 2.28 Å, ca. 1.1 Å less than twice the van der Waals radius for carbon, so that there is no possibility of independent rotation of the  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}$  groups around the C–Zn–C linkage without substantial adjustment of the geometry within each group.

The values of the Si–O–Me angle ( $122.0(4)^\circ$ ) and the length of the Si–O bond ( $1.674(3)\text{Å}$ ) are respectively at the lower and upper ranges noted for 127 species containing Si–O–C<sub>*s,p*</sub> fragments, for which the average bond angle was  $134.2^\circ$  and average Si–O bond length 1.62 Å [8].

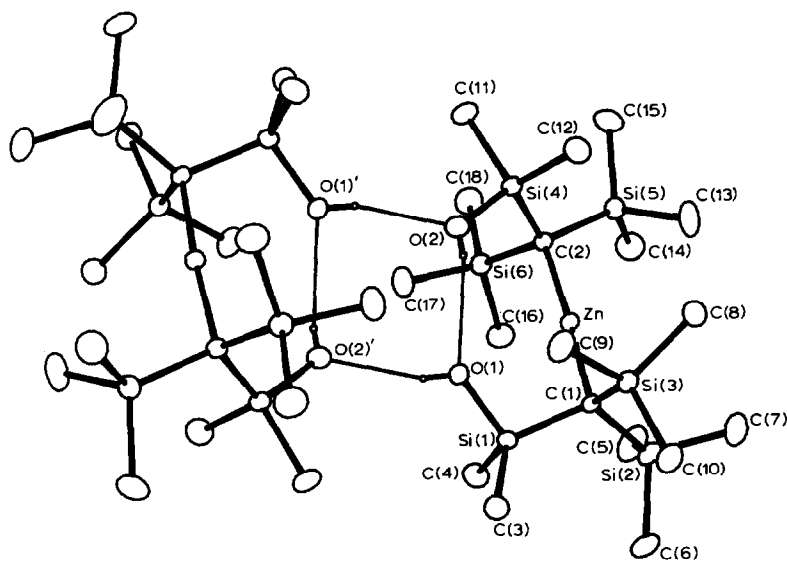


Fig. 3. Structure of  $[(\text{HOME}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$ , **2**, with atom numbering.

*Crystal structure of the diol 2*

The solid state structure of **2** was found to be markedly different from those of **1** and **3**, as can be seen from Fig. 3. The crystal consists of hydrogen-bonded dimers. There is a hydrogen bond between the two oxygen atoms within each molecule, and

Table 4

Intramolecular distances (Å) and angles (°) in the diol **2**, with estimated standard deviations in parentheses <sup>a</sup>

<b>(a) Bonds</b>			
Zn–C(1)	1.965(2)	Zn–C(2)	1.970(2)
Si(1)–O(1)	1.663(2)	Si(1)–C(1)	1.858(3)
Si(1)–C(3)	1.861(3)	Si(1)–C(4)	1.861(4)
Si(2)–C(1)	1.883(3)	Si(2)–C(5)	1.858(4)
Si(2)–C(6)	1.881(4)	Si(2)–C(7)	1.869(4)
Si(3)–C(1)	1.891(3)	Si(3)–C(8)	1.864(4)
Si(3)–C(9)	1.865(3)	Si(3)–C(10)	1.871(3)
Si(4)–O(2)	1.658(2)	Si(4)–C(2)	1.868(3)
Si(4)–C(11)	1.862(3)	Si(4)–C(12)	1.864(4)
Si(5)–C(2)	1.881(3)	Si(5)–C(13)	1.859(4)
Si(5)–C(14)	1.874(4)	Si(5)–C(15)	1.866(3)
Si(6)–C(2)	1.891(3)	Si(6)–C(16)	1.871(4)
Si(6)–C(17)	1.857(4)	Si(6)–C(18)	1.878(3)
O(1)–H(1)	0.74(3)	O(2)–H(2)	0.60(2)
H(1)⋯O(2)′	2.12(3)	H(2)⋯O(1)	2.35(3)
<b>(b) Angles</b>			
C(1)–Zn–C(2)	175.9(1)	O(1)–Si(1)–C(1)	103.7(1)
O(1)–Si(1)–C(3)	110.8(1)	O(1)–Si(1)–C(4)	105.8(1)
C(1)–Si(1)–C(3)	114.5(1)	C(1)–Si(1)–C(4)	115.4(1)
C(3)–Si(1)–C(4)	106.4(2)	C(1)–Si(2)–C(5)	112.4(2)
C(1)–Si(2)–C(6)	112.3(1)	C(1)–Si(2)–C(7)	113.0(2)
C(5)–Si(2)–C(6)	107.2(2)	C(5)–Si(2)–C(7)	105.5(2)
C(6)–Si(2)–C(7)	105.8(2)	C(1)–Si(3)–C(8)	113.0(1)
C(1)–Si(3)–C(9)	112.5(1)	C(1)–Si(3)–C(10)	113.1(1)
C(8)–Si(3)–C(9)	105.1(2)	C(8)–Si(3)–C(10)	105.9(2)
C(9)–Si(3)–C(10)	106.5(1)	O(2)–Si(4)–C(2)	111.1(1)
O(2)–Si(4)–C(11)	103.2(1)	O(2)–Si(4)–C(12)	106.9(1)
C(2)–Si(4)–C(11)	115.4(1)	C(2)–Si(4)–C(12)	113.2(1)
C(11)–Si(4)–C(12)	106.2(2)	C(2)–Si(5)–C(13)	112.5(1)
C(2)–Si(5)–C(14)	114.1(2)	C(2)–Si(5)–C(15)	113.0(1)
C(13)–Si(5)–C(14)	104.4(2)	C(13)–Si(5)–C(15)	106.8(2)
C(14)–Si(5)–C(15)	105.3(2)	C(2)–Si(6)–C(16)	112.7(1)
C(2)–Si(6)–C(17)	113.4(1)	C(2)–Si(6)–C(18)	112.4(2)
C(16)–Si(6)–C(17)	104.5(2)	C(16)–Si(6)–C(18)	106.4(2)
C(17)–Si(6)–C(18)	106.7(2)	Si(1)–O(1)–H(1)	121(2)
Si(4)–O(2)–H(2)	119(2)	Zn–C(1)–Si(1)	99.5(1)
Zn–C(1)–Si(2)	110.2(1)	Zn–C(1)–Si(3)	108.3(1)
Si(1)–C(1)–Si(2)	114.9(2)	Si(1)–C(1)–Si(3)	111.0(1)
Si(2)–C(1)–Si(3)	112.1(1)	Zn–C(2)–Si(4)	103.5(1)
Zn–C(2)–Si(5)	107.5(1)	Zn–C(2)–Si(6)	108.0(1)
Si(4)–C(2)–Si(5)	113.3(2)	Si(4)–C(2)–Si(6)	111.8(1)
Si(5)–C(2)–Si(6)	112.1(1)	O(2)–H(2)⋯O(1)	156(3)
O(1)–H(1)⋯O(2)′	162(3)		

<sup>a</sup> Symmetry element ′ is:  $-x, -y, 1-z$ .

there are two such bonds to the oxygens of another molecule. There is only one dimer in the unit cell. The bond lengths and angles are listed in Table 4. The main features of the structure are as follows:

(a) In contrast to all other structurally characterized compounds of the types  $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{M}$ ,  $[\{(\text{Me}_3\text{Si})_3\text{C}\}_2\text{M}]^-$ , and  $[(\text{XMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{M}$  (for details see Table 2), in which the metal atoms lie on an inversion centre and the C–M–C linkage is thus linear, in compound **2** the C–Zn–C linkage is slightly bent, the angle being  $175.9(1)^\circ$ . The non-linearity can be attributed to the hydrogen bonding, which draws together the two OH groups and their associated  $\text{SiMe}_2$  entities.

(b) The intramolecular  $\text{O} \cdots \text{O}$  distance,  $2.910(3) \text{ \AA}$ , is slightly longer than the intermolecular  $\text{O} \cdots \text{O}$  distance,  $2.831(3) \text{ \AA}$ . Both hydrogen bonds are markedly bent, the  $\text{O}–\text{H} \cdots \text{O}$  angle being  $156(3)^\circ$  for the intramolecular bond and  $162(3)^\circ$  for the intermolecular bond.

(c) Because the two OH groups within each molecule are inequivalent, one oxygen atom, O(2), donating its hydrogen atom intramolecularly and accepting a hydrogen atom intermolecularly, and the other, O(1), showing the complementary behaviour, the two halves of the molecule are significantly dissimilar. The main obvious differences are in the values of the C(1)–Si(1)–O(1) and C(2)–Si(4)–O(2) angles ( $103.7(1)$  and  $111.1(1)^\circ$ , respectively) and the Zn–C(1)–Si(1) and Zn–C(2)–Si(4) angles ( $99.5(1)$  and  $103.5(1)^\circ$ ), but perhaps more significant are the differences in the  $\text{O}(1) \cdots \text{Zn}$  and  $\text{O}(2) \cdots \text{Zn}$  distances ( $2.846(2)$  and  $3.273(2) \text{ \AA}$ , respectively). The  $\text{O}(1) \cdots \text{Zn}$  distance is slightly less than the sum ( $2.90 \text{ \AA}$ ) of the van der Waals radii for O and Zn: as in the case of **2**, this relatively close approach may reflect a weak interaction, but it is more likely to originate in minimization of steric strain in the very crowded molecule. The atom O(2) cannot approach in the Zn atom in this way because of the orientation of its associated hydrogen atom.

(d) The Zn–C bond lengths,  $1.965(2)$  and  $1.970(2) \text{ \AA}$ , are not significantly different from that in  $[\{(\text{Me}_2\text{PhSi})_3\text{CZnOH}\}_2]$ ,  $1.953(7) \text{ \AA}$  [17], or those in the compounds  $[(\text{XMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$  with  $\text{X} = \text{Cl}$ ,  $\text{OMe}$ , or  $\text{O}_2\text{CCF}_3$  (see Table 3). They are the shortest so far observed for compounds of the types  $[(\text{XMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{M}$  and  $[\{(\text{Me}_3\text{Si})_3\text{C}\}_2\text{M}]^-$ , as can be seen from Table 3.

(e) The  $(\text{Me}_3\text{Si})_3\text{C}$  entities show features noted previously in compounds containing  $(\text{Me}_3\text{Si})_3\text{C}$  or related groups [14]. For example, within the C(2)–Si(5) $\text{Me}_3$  system, the C(2)–Si(5) bond length,  $1.881(1) \text{ \AA}$ , is slightly greater than that of the Si–Me bonds (mean  $1.866(7) \text{ \AA}$ ), and the C–Si–Me angles (mean  $113.3(8)$ ) are significantly greater and the Me–Si–Me angles (mean  $105.8(12)$ ) correspondingly less than the tetrahedral value.

## Experimental

### Preparations

The preparation of the zinc compounds **1** and **2** will be described elsewhere (cf. ref. 1). The mercury compound **3** was obtained by the sequence described below.

(i) A  $2.6 \text{ M}$  solution of  ${}^n\text{BuLi}$  ( $0.106 \text{ mol}$ ) in *n*-hexane cooled to  $-78^\circ\text{C}$  was added dropwise during 1 h to a stirred solution of  $(\text{Me}_3\text{Si})_2\text{CCl}_2$  ( $25 \text{ g}$ ,  $0.11 \text{ mol}$ ) in THF ( $100 \text{ cm}^3$ ), ether ( $12.5 \text{ cm}^3$ ), and *n*-pentane ( $10 \text{ cm}^3$ ) cooled to  $-110^\circ\text{C}$ . The mixture was stirred for 30 min at  $-110^\circ\text{C}$  and then  $\text{Me}_2\text{SiClH}$  ( $11.5 \text{ g}$ ,  $0.10 \text{ mol}$ ) cooled to  $-78^\circ\text{C}$  was added dropwise with stirring. The mixture was allowed to

warm to room temperature then treated carefully with an excess of aqueous ammonium chloride. The solvent was evaporated off under reduced pressure, and unchanged  $(\text{Me}_3\text{Si})_2\text{CCl}_2$  was distilled from the residue (b.p. ca.  $99^\circ\text{C}$  at 30 Torr) to leave a solid. This was recrystallized from MeOH to give  $(\text{HMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCl}$  (15 g, 59%), m.p.  $111^\circ\text{C}$ ;  $\delta_{\text{H}}$  (in  $\text{CCl}_4$ ) 0.18 (s, 18H, SiMe<sub>3</sub>), 0.27 (d, 6H, SiMe<sub>2</sub>H), and 4.11 (m, 1H, SiH).

(ii) A 1.0 M solution of Br<sub>2</sub> (30 mmol) in  $\text{CCl}_4$  (30 cm<sup>3</sup>) was added dropwise to a stirred solution of  $(\text{HMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCl}$  (4.26 g, 17 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 cm<sup>3</sup>) at room temperature. The mixture was stirred for 20 min and the solvent was then removed under reduced pressure to leave a solid, which was sublimed ( $70^\circ\text{C}$  at 0.05 Torr) to give  $(\text{BrMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCl}$  (5.0 g, 90%), m.p.  $197^\circ\text{C}$ ;  $\delta_{\text{H}}$  0.30 (s, 18H, SiMe<sub>3</sub>), and 0.75 (s, 6H, SiMe<sub>2</sub>Br).

(iii) A solution of  $(\text{BrMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCl}$  (4.0 g, 12.1 mmol) in a mixture of  $\text{CH}_2\text{Cl}_2$  (40 cm<sup>3</sup>) and MeOH (10 cm<sup>3</sup>) was stirred at room temperature for 20 h (probably an unnecessarily long time) and the solvent was then removed under reduced pressure to leave a white solid, which was sublimed ( $60^\circ\text{C}$  at 0.05 Torr) to give  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCl}$  (3.07 g, 90%), m.p.  $118^\circ\text{C}$ ;  $\delta_{\text{H}}$  0.18 (s, 18H, SiMe<sub>3</sub>), 0.25 (s, 6H, SiMe<sub>2</sub>OMe), and 3.43 (s, 3H, OMe).

(iv) A stirred solution of  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCl}$  (2.0 g, 7.1 mmol) in THF (50 cm<sup>3</sup>) was treated dropwise with <sup>n</sup>BuLi (7.1 mmol) in hexane (2.7 cm<sup>3</sup>) at  $-110^\circ\text{C}$ . After 45 min additional stirring the mixture was transferred to a Drikold-cooled dropping funnel and added dropwise to a stirred mixture of HgBr<sub>2</sub> (1.3 g, 3.55 mmol) and THF (10 cm<sup>3</sup>) at  $-110^\circ\text{C}$ . The mixture was allowed to warm to room temperature, the solvent was removed under vacuum, and the solid residue was extracted with pentane. The extract was filtered and the solvent removed under nitrogen to leave a solid, which was recrystallized from MeOH and shown to be  $[(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Hg}$ , (0.74 g, 30%), m.p.  $212\text{--}214^\circ\text{C}$ ;  $\delta_{\text{H}}$  0.13 (s, 36H, SiMe<sub>3</sub>), 0.24 (s, 12H, SiMe<sub>2</sub>OMe), and 3.43 (s, 6H, OMe) (Found: C, 34.6; H, 7.8.  $\text{C}_{20}\text{H}_{54}\text{O}_2\text{Si}_6\text{Hg}$  calcd.: C, 34.5; H, 7.8%);  $\delta_{\text{Hg}}$   $-563.6$  ppm relative to HgMe<sub>2</sub>;  $m/z$  (EI, 70 eV) 696 (5%,  $[M]^+$ ), 681 (80,  $[M - \text{Me}]^+$ ), 449 (10,  $[(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CHg}]^+$ ), 333 (25), 247 (20), 232 (100,  $[(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C} - \text{Me}]^+$ ), 219 (95), 187 (30), 129 (15), 89 (20), 60 (10). (All mercury-containing ions showed the expected isotope pattern.)

### Structure determinations

In all three cases data were collected on an Enraf–Nonius CAD4 diffractometer, with intensities measured by a  $\theta$ – $2\theta$  scan with a scan width  $\Delta\theta = (0.8 + 0.35 \tan \theta)^\circ$ , and a maximum scan time of one min. Programs from the Enraf–Nonius SDP-Plus package were run on a MicroVax computer. The values of  $\sigma(F^2)$  were calculated as  $[\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$ . Lists of thermal parameters and structure factors are available from P.B.H.

### $[\text{HOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$ , 2

Suitable crystals were obtained by recrystallization from pentane.

*Crystal data.*  $\text{C}_{18}\text{H}_{50}\text{O}_2\text{Si}_6\text{Zn}$ ,  $M = 532.5$ , triclinic,  $a = 9.324(2)$ ,  $b = 11.275(3)$ ,  $c = 15.708(2)$  Å,  $\alpha = 80.39(2)$ ,  $\beta = 85.25(1)$ ,  $\gamma = 70.95(2)^\circ$ ,  $U = 1538.2$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.29$  g cm<sup>-3</sup>,  $F(000) = 576$ . Monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 10.5$  cm<sup>-1</sup>. Space group  $P\bar{1}$ , from successful structure refinement.



Table 5

Fractional atomic coordinates ( $\times 10^4$ ,  $\times 10^3$  for H) for the diol **2**, with estimated standard deviations in parentheses

	x	y	z
Zn	1798.4(3)	-19.9(3)	2569.4(2)
Si(1)	609.1(9)	2459.9(7)	3144.8(5)
Si(2)	1842.7(9)	2377.9(8)	1218.1(5)
Si(3)	-1230.1(8)	1887.7(7)	1807.2(5)
Si(4)	1191.1(8)	-2283.7(7)	3657.5(5)
Si(5)	3667.5(10)	-2709.3(8)	2165.5(5)
Si(6)	4251.5(9)	-1816.0(7)	3849.6(5)
O(1)	274(2)	1369(2)	3915(1)
O(2)	179(2)	-1222(2)	4271(1)
C(1)	722(3)	1767(2)	2139(2)
C(Q)	2787(3)	-1795(2)	3079(2)
C(3)	-895(5)	4021(3)	3162(2)
C(4)	2397(4)	2669(3)	3434(2)
C(5)	3924(4)	1676(4)	1359(3)
C(6)	1377(5)	4151(3)	1081(3)
C(7)	1488(4)	2011(4)	153(2)
C(8)	-1193(4)	680(3)	1120(2)
C(9)	-2500(3)	1634(4)	2752(2)
C(10)	-2240(4)	3464(3)	1176(2)
C(11)	1766(4)	-3785(3)	4434(2)
C(12)	-152(4)	-2473(3)	2915(2)
C(13)	2504(5)	-2145(4)	1184(2)
C(14)	5577(4)	-2585(4)	1782(3)
C(15)	3959(4)	-4444(3)	2449(3)
C(16)	5431(4)	-788(3)	3386(3)
C(17)	3411(4)	-1212(4)	4868(2)
C(18)	5613(4)	-3451(3)	4165(3)
H(1)	11(3)	149(3)	437(2)
H(2)	2(3)	-67(2)	413(2)

A crystal of ca.  $0.6 \times 0.15 \times 0.10$  mm was used. Intensities for 5392 unique reflections with  $+h \pm k \pm l$  and  $2 < \theta < 25^\circ$  were measured. After correction for Lorentz and polarization effects, but not for absorption, 4302 reflections with  $|F|^2 > \sigma(F^2)$  were used for the structure analysis.

A Patterson map was used to locate the Zn atom and a difference map to find the Si, O, and C atoms, which were all refined by full matrix least squares with anisotropic temperature factors. The hydrogen atoms were found on a difference map and refined isotropically. Refinement converged at  $R = 0.033$ ,  $R' = 0.040$  with weighting scheme  $w = 1/\sigma^2(F)$ . A final difference map was everywhere  $< 0.3 \text{ e}\text{\AA}^{-3}$ . The final atomic coordinates are given in Table 5.

#### $[(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Zn}$ , **1**

Suitable crystals were obtained by recrystallization from MeOH.

*Crystal data.*  $\text{C}_{20}\text{H}_{34}\text{O}_2\text{Si}_6\text{Zn}$ ,  $M = 560.5$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.283(6)$ ,  $b = 17.393(7)$ ,  $c = 10.407(3)$  Å,  $\beta = 104.88(4)^\circ$ ,  $U = 1623.9$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.1 \text{ g cm}^{-3}$ ,  $F(000) = 608$ . Monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$ , Å,  $\mu = 10.1 \text{ cm}^{-1}$ .

Table 6

Fractional atomic coordinates ( $\times 10^4$ ) for **1** with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Zn	0	0	0
Si(1)	-610(1)	1226(1)	1912(1)
Si(2)	2372(1)	295(1)	2692(1)
Si(3)	1821(1)	1469(1)	381(1)
O	727(4)	1435(2)	-1172(3)
C(1)	953(4)	786(2)	1324(3)
C(2)	-1965(6)	489(4)	2174(5)
C(3)	-1745(6)	1919(3)	680(6)
C(4)	41(6)	1755(4)	3534(5)
C(5)	1560(7)	-223(3)	3894(5)
C(6)	3436(6)	-450(3)	2036(5)
C(7)	3776(6)	981(3)	3701(5)
C(8)	3729(6)	1217(3)	259(5)
C(9)	1949(6)	2483(3)	1027(7)
C(10)	1062(9)	1846(5)	-2215(7)

A crystal of ca.  $0.4 \times 0.3 \times 0.2$  mm was used. Intensities for 2787 unique reflections with  $+h + k \pm l$  and  $2 < \theta < 25^\circ$  were measured. After correction for Lorentz and polarization effects, but not for absorption, 1897 reflections with  $|F|^2 > \sigma(F^2)$  were used for the structure analysis.

The Zn atom lies on an inversion centre, and the C, O, and Si atoms were found on a difference map and refined by full matrix least squares with anisotropic temperature factors. The hydrogen atoms were found on a difference map except for those attached to C(6), which were fixed at calculated positions, and the hydrogen atoms on C(10), which were omitted. The hydrogen atoms were refined with isotropic temperature factors. Refinement converged at  $R = 0.042$ ,  $R' = 0.049$ . A final difference map had peaks of up to  $0.3 \text{ e}\text{\AA}^{-3}$ . The atomic coordinates are given in Table 6.

### $[(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Hg}$ , **3**

Suitable crystals were obtained by recrystallization from MeOH.

*Crystal data.*  $\text{C}_{20}\text{H}_{54}\text{HgO}_2\text{Si}_6$ ,  $M = 695.8$ , monoclinic, space group  $C2/c$ ,  $a = 16.797(11)$ ,  $b = 9.354(8)$ ,  $c = 22.948(8)$  Å,  $\beta = 108.71(4)^\circ$ ,  $U = 3415.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.35 \text{ g cm}^{-3}$ ,  $F(000) = 1416$ . Monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 47.3 \text{ cm}^{-1}$ .

A very thin plate of ca.  $0.5 \times 0.5 \times 0.025$  mm was used. A total of 2999 unique reflections were measured for  $2 < \theta < 25^\circ$  and  $+h + k \pm l$ , and 1738 with  $|F|^2 > 3\sigma(F^2)$  were used for the refinement. There was no crystal decay. An absorption correction was made using DIFABS [18] after isotropic refinement.

The structure was solved by routine heavy atom methods and refined by full matrix least squares with non-hydrogen atoms anisotropic, except for C(10), which became non-positive definite when anisotropic and was therefore left isotropic. Hydrogen atoms were omitted. The Si atoms were disordered between two alternative orientations, and the relative occupancies refined to 0.75/0.25. The weighting scheme was  $w = 1/\sigma^2(F)$  and the final residuals were  $R = 0.067$ ,  $R' = 0.084$ . A

Table 7

Fractional atomic coordinates ( $\times 10^4$ ) for 3, with estimated standard deviations in parentheses

	x	y	z	
Hg	2500	2500	5000	
Si(1)	3110(7)	3702(12)	6392(5)	occupancy 0.75
Si(2)	1593(7)	1621(16)	5959(5)	
Si(3)	3441(8)	493(13)	6158(5)	
O(1)	4548(19)	1250(43)	6430(14)	
C(1)	2651(14)	2095(20)	5916(9)	
C(2)	3670(19)	3409(36)	7212(12)	
C(3)	2154(22)	5097(38)	6279(15)	
C(4)	3874(17)	4665(39)	6101(13)	
C(5)	806(20)	2862(35)	5498(14)	
C(6)	1478(18)	1881(40)	6753(11)	
C(7)	1329(21)	-415(38)	5659(16)	
C(8)	3221(19)	-818(29)	5511(13)	
C(9)	3303(27)	-476(27)	6895(12)	
C(10)	4726(40)	2278(85)	5835(30)	
Si(1a)	3651(14)	2819(26)	6382(11)	occupancy 0.25
Si(2a)	2539(18)	97(29)	5959(12)	
Si(3a)	1701(16)	3076(29)	6079(12)	

final difference map had residual density of up to  $1.4 \text{ e}\text{\AA}^{-3}$  near the Hg atom. The atomic coordinates are given in Table 7.

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